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# *Report of the Materials Research Council (1976)*

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# REPORT

## OF

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(10) M. J. Sinnott

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## INTRODUCTION

This report is a summary of the activities of the
Materials Research Council during its annual Summer Conference
held in La Jolla, California, during the period July 6-30, 1976.
A more complete presentation of the technical papers, workshop
reports and memoranda generated by the Council will be prepared
and issued later in the contract year.

The Materials Research Council was organized by the
Materials Science Office of the Defense Advanced Research
Projects Agency to assist them in examining potential future
materials problem areas of the Department of Defense. It is not
directly concerned with current problems, although it has and
will continue to work on these when it can be of assistance.
Its primary function is to look beyond the current problems to
those of the future and to suggest possible studies that will
insure that the necessary science base and preliminary engineer-
ing feasibility studies are in place to support later engineering
and system development.

The membership of the Council is made up of ceramists,
chemists, physicists and engineers whose common interests lie
in materials science or materials engineering. This meeting of
the Council was the ninth year of operation and over this period
this diverse group of scientists and engineers have developed

into one of the most knowledgeable and versatile consultant groups in the Country.

Since most of the Council membership is drawn from the academic community, their early exposure to emerging materials problems results in their prompt transfer, via their graduate students, into active research programs. Support of these programs comes from several sources, not just the Department of Defense. NSF, ERDA, Industries, Universities and Technical Associations are all represented in the support of these research programs. The range of these programs is very broad since it covers all of the topics that have been examined by the Council over the last several years. Currently work is going on in acoustic scattering, epitaxy, fracture, surface chemistry, non-equilibrium structures, structural ceramics, wear, etc.

While the Council has considerable expertise in many areas, it draws heavily from the science and engineering communities for consultants, assistance and advice. These come from government agencies, industrial laboratories, not-for-profit institutions and from universities. Visitors who have a special interest and capabilities in the areas under consideration by the Council are encouraged to attend and take part in the briefings and discussions that make up part of the Summer Conference of the Council. Visitors have included NSF and NBS personnel, representatives of the basic research offices of the three services; AFOSR, ARO, and ONR and other DoD research and development groups such as NRL, AMMRC, AFML, AFWL, NSRDC, NSWL,

etc.  These service personnel perform a particularly valuable function since they have an intimate knowledge of on-going current research and can relate it to the advanced research concepts under consideration of the Council to the benefit of both groups.

## PROJECT ORGANIZATION

The technical direction of the Materials Research Council is delegated to a seven-man Steering Committee chosen to represent the various disciplines of the Council membership.  Membership on the Steering Committee is usually for a period of three years with replacements made each year.

The functions of the Steering Committee are:

a) Work with ARPA-MATS to select problem areas for consideration by the Council.

b) Select Council members, specialists and consultants to work with the Council.

c) Structure, direct and evaluate Council activities.

d) Participate in project management.

The current Steering Committee is as follows:

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There are many people qualified for Council membership but budgetary considerations limits the numbers to 20-25. To obtain a greater flexibility in membership, a recent policy was instituted where some of the Council members are asked to go on an inactive status and new members are added. Some members, because of other commitments, elect to be placed on the inactive list. Inactive members are usually recalled to membership as the Council moves back into their areas of expertise. The current inactive list of Council members is as follows:

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## ORGANIZATION OF THE SUMMER CONFERENCES

The principal function of the Materials Research Council is to provide ARPA with a variety of services which bear on the development and use of materials in defense systems. The vehicle for providing these services is the Summer Conference which is a one month summer study meeting.

During the summer meeting the Council not only carries out research of an analytic nature, but also holds conferences and workshops devoted to themes of mutual interest to the Council and ARPA with a balance being sought between themes suggested by ARPA and those suggested by the Council. Position papers are prepared after the conferences and workshops, to aid ARPA in judging the pertinence of new programs, in stimulating the generation of such programs, or in assisting in the evolution of new scientific concepts. A secondary aim is the stimulation

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of the research efforts of individual scientists and engineers who participate in these meetings. Workshops are attended by Council members, who may not be expert in the subject under discussion, and by a core of experts, usually non-Council members, who are selected and invited by the Steering Committee to lead the discussion. The philosophy under which Council members participate in conferences outside their customary interests is based on the idea that highly competent scientists, even if not experts in that field, can bring fresh ideas to that field by virtue of their competence and the fact that they may not be committed to firm and sometimes controversial points of view.

Several techniques for conducting the summer conference have been implemented during its nine years of operation. Initially the entire MRC membership focused on a few problems presented to them via briefings from the various segments of the Services or DoD agencies. Typical topics covered were: Shock Propagation, Constitutive Relations at High Temperature and Pressure, Composite Materials and Underground Sensing. From this the Council evolved a technique whereby individual Council members were given the responsibility of structuring conferences or workshops that would be of interest to different subsets of the Council. Meetings have been held on such topics as Amorphous Semiconductors, Infrared Optics, Materials in Energy Systems, Structural Ceramics, etc.

Because of continuing interest from year to year of the individual members in certain topics, there is a considerable

carry-over from one conference to the next of the various study areas. Over the nine year period, of the order of twenty major studies have been carried out in areas such as: Composite Materials, Biomaterials, Laser Optics, Superconducting Materials, Solid Electrolytes, Wear, Erosion, Fracture. From these major studies, smaller groups of the Council have nucleated studies in spin-off areas that are more suited to their particular expertise and they regularly report back to the Council the new developments, refinements in theories, experimental studies, new applications, etc.

Output from the Council appears in two publications. The Preliminary Report gives in summary form the results of the Summer Conference. The Final Report, issued later in the year, contains all the written output of the Council. Much of the Final Report consists of technical papers ready for publication in appropriate journals. The balance are preliminary reports and memoranda generated primarily for distribution within the Council and to its consultants. They serve to stimulate discussion since they are initial position papers and present tentative unrefined concepts and ideas. Their distribution is restricted since they do not represent a unanimous or even a consensus opinion of the Council. They are available on request to the Project Director, subject to the author's release.

## SUMMER CONFERENCE - 1976

In preparation for the 1976 Summer Conference, the Steering Committee met in Washington, D.C., on November 21, 1976, with the Staff of ARPA-MATS. Input from the Council was available on possible study topics. Topics were also submitted by ARPA-MATS. From the rather extensive list considered, the following topics were tentatively chosen and a Council member was assigned to structure the program, invite participants, and to collect pertinent publications for distribution to interested Council members.

1. Pyroelectric and Piezoelectric Materials
     Professor Kino

2. Non-Destructive Evaluation
     Dr. Thomson

3. Fatigue Crack Growth
     Professors Budiansky, Rice

4. Epitaxial Films
     Professor Yariv

5. Fine Metal Powder Technology
     Professors Cohen, Hirth, Hucke

6. Metallic Glasses
     Dr. Gilman

It was agreed that the formal presentations of the problems by experts should be restricted to one or two days at most and suitable time left for discussion, argumentation and analysis by Council members.

ARPA-MATS indicated that they would probably schedule a review of potential optical fiber problems in cooperation with the Naval Electronics Laboratory.

The Steering Committee met again in Washington, D.C., on February 28th with ARPA-MATS personnel to review the plans for the 1976 Summer Conference. The agenda for the six meetings were approved after some rearrangement of timing of the workshops to avoid overlapping of presentations. ARPA-MATS indicated that it would, in addition to the review on optical fibers, probably schedule a one day meeting on metal-matrix composites in cooperation with J. Persh of ODDRE. They also indicated that, if time permitted, they would like the Council to look into the area of high-pressure research.

In March a newsletter was circulated to the entire Council giving the agenda of the summer program. The general policy of the MRC has been to schedule all conferences and workshops into the first two weeks of the Summer Conference in order to give the membership time in the final two weeks to prepare meeting summaries, discuss the presentations with other members and to prepare the papers to be published in the Preliminary and Final Reports of the program. This timing generally produces some overlap in the scheduling of the meetings. ARPA-MATS requested that this policy be relaxed and that some of the meetings be scheduled into the third week to enable their personnel to attend all of the meetings. This was approved, although it was pointed out that this might adversely affect the Council output.

The actual agenda of the 1976 Summer Conference was as follows:

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July 6            Conference opened
July 7-8          Pyro- and piezoelectric materials
July 7-8-9        Fatigue crack growth
July 8-9          ARPA-AFML NDE programs
July 12-13        Epitaxial films
July 12-13-14     Acoustic scatterers, NDE
July 14-15-16     Fine powder technology
July 15-16        Ceramic turbine advisory panel
July 19-20        Metallic glasses
July 21-22        Optical fibers
July 26           Metal matrix composites
July 30           Conference closed
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In spite of the prior planning there was considerable overlap on the conferences. This is almost unavoidable since the availability of the experts is the real determining factor in fixing the calendar.

The individual meetings were well attended and quite productive in spite of their large number. Not all of the meetings were attended by all of the MRC members. Each member selects a few in which he has an interest and to which he can contribute. There is probably an optimum in the number of conferences that can be held at the summer meeting. In earlier meetings two or three topics were considered and this was too few; the 1976 meeting probably had too many. The Steering Committee will attempt to find a better balance.

The following pages present the summary of the meetings; the agenda and a listing of the participants and visitors. In some some cases abstracts of the papers presented have been included. The Final Report will include an expanded treatment of this material.

CONFERENCE ON PYROELECTRIC AND PIEZOELECTRIC MATERIALS

SUMMARY

G. S. Kino

Three classes of materials were reviewed; pyroelectric
materials suitable for use in infrared vidicon devices, piezo-
electric ceramics and piezoelectric and pyroelectric organic
polymers.

Well developed 100-200 line infrared vidicons are now
obtainable commercially, and were described by Singer and
Helmick. They have a sensitivity of 0.3°C-0.5°C at the target
and appear to be operating near their estimated thermodynamic
limit for the target materials used. Further improvements
depend on the use of thinner retinas and somewhat more sensitive
readout techniques. The pyroelectric figure of merit of proper
ferroelectrics was shown by Liu and Bell to be near its theoreti-
cal limit.

The new pyroelectric and piezoelectric polymers have many
potential advantages. They are tough, flexible and cheap. The
pyroelectric figure of merit of these materials is a factor of
2 or 3 worse than the more conventional materials. As piezo-
electrics, these materials have very desireable characteristics:
a good coupling coefficient and a low acoustic impedance near
that of water. High quality, broad band acoustic transducers,
comparable to the best available commercial ceramic devices were
described by Shaw.

There should be a large class of these materials still
to be developed and research on these materials should be en-
couraged.  New device applications as well as the more obvious
conventional ones should be studied and developed.

The work on PZT ceramics appears to be at a mature stage.
Further improvements are possible but unlikely to be carried out
in industry due to the large market in cheap uncritical consumer
components.  A particular need is better uniformity from sample
to sample which could probably be obtained by better processing.

Other applications of ceramics were discussed, in particu-
lar the optical memory devices of Land and Fresnel lenses of Auld.
The optical memory device work should be continued.

Some attention was paid to the so-called improper ferro-
electrics.  These materials have a figure of merit which does not
obey the same criteria as do the proper ferroelectrics.  They
might provide some improvement in pyroelectric vidicons.  A small
effort in this field would be worthwhile.

Abstracts of the individual papers presented at this
conference will be published in the Final Report.

CONFERENCE ON PYROELECTRIC AND PIEZOELECTRIC MATERIALS

July 7-8, 1976

AGENDA

Introduction - G. S. Kino

Electronic Processes in Pyroelectric Materials - A. Glass

Recent Developments in Pyroelectric Vidicon Systems - C. Helmick
        and W. Woodworth

Vidicon Arrays - T. Conklin, G. Loiancono and B. Singer

Performance Limitations of Pyroelectric Detectors - S. T. Liu

Theory of Pyroelectricity - M. Bell

Pyroelectric Polymers - A. Glass and J. B. Lando

Study of Ultrasonic Resonance and Broadband Transduction in
    $PVF_2$ Piezoelectric Film - H. J. Shaw

Piezoelectric Materials - L. E. Cross

Piezoelectric Ceramic Materials and Their Application in Devices -
            D. Berlincourt

Processing of Polycrystalline Piezoelectric Ceramics in the PZT
    System - R. Fulrath

Acoustic Wave Guiding Along Piezoelectric Domain Wall Boundaries -
            B. A. Auld

PLZT Materials Properties of Importance to Information Storage
and Display Applications - C. A. Land

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WORKSHOP ON THE THEORY OF ULTRASONIC SCATTERING
WITH APPLICATION TO ADAPTIVE COMPUTERIZED NDE

R. M. Thomson

## SUMMARY

A week long workshop explained the current prospects
for characterization of defects in solids by combining the
most advanced features of elastic wave scattering theory, the
current experimental capability, and computer adaptive tech-
niques.  The current status of these three areas was reviewed
and papers were prepared detailing advances, partially worked
out at the MRC, which could be made in this direction.  The
general concensus of the workshop was that the goal was a
feasible one for the relatively short term because of the power
of present concepts and capabilities in the three areas.

CONFERENCE ON THEORY OF ULTRASONIC SCATTERING

July 12-15, 1976

Comparisons of Theory and Experiment in Ultrasonic Scattering
        B. Thompson

Ultrasonic Transducers
        G. Kino

Computer Analysis of Acoustic Signals
        A. Mucciardi

Review of Theory
        E. A. Kraut

Review of Gubernatis-Krumhansl Analysis
        J. E. Gubernatis

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WORKSHOP ON NDE

M. Buckley and R. Thomson

## SUMMARY

A two-day workship was held at the MRC site to explore
issues in the NDE area of potential concern or interest to ARPA.
Specific areas studied were NDE for adhesive bonding and com-
posites, NDE for fatigue damage detection, automation in NDE,
and the institutional framework of R&D in NDE.

The most significant issue to surface at the workshop
was the need to exploit the full physical capability of NDE
through an extensive application of computerized automation for
overall nondestructive quality evaluation.  Without such a
development, NDE is likely to remain unreliable, slow, unable
to correlate data from a large number of parallel inputs, and
expensive.  Integration of the NDE community with the electronic
and computer communities is an excellent opportunity for pro-
moting further advancements in both fields.

We also found significant R&D technical challenges im-
bedded in the adhesive bonds, composites and fatigue areas.
Specifically, NDE for adhesive handling will require considerable
effort to establish practical methods for sensing the adhesive
bond strength, but some techniques which are sensitive to the

cohesive strength of the adhesive already show considerable promise. A big gap appears in the development and application area of NDE for adhesive bonds, especially as it bears on the AF PABST program. (The PABST program is an ambitious attempt on the part of the Air Force to substitute adhesives for mechanical fasteners and rivets in primary aircraft structures.) In order to bring NDE for composites to the level now current in the metals area, considerable research coupling NDE to research on fundamental failure modes in composites will be required. Under institutional issues, the desirability of a centralized NDE center was explored. We conclude that the central issue in this area is to provide sufficient stability for the research community now developing through the auspices of the AF/ARPA program and elsewhere in order for it to gain maturity. A centralized laboratory is one of probably several possible routes for the exploration of this maturity. The development of an integrated NDE service industry was discussed, and is believed sufficiently attractive that we reopen it for further study and consideration, especially as it bears on the automation issue mentioned earlier.

A more complete report on the details of the workshop will appear in the Final Report of the Summer Conference.

CONFERENCE ON NON-DESTRUCTIVE EVALUATION

PROGRAM SCHEDULE

July 8, 9, 1976


Introductory Remarks - R. Thomson

Current ARPA-AF Program in NDE
    M. Buckley and D. Thomson

NDE for Adhesive Bonding and Composites
    W. Yee, J. Florence, D. Hagemaier

Automation in NDE
    D. Ballard, J. Bushnell, W. Coleman, D. Green

Fatigue Detection
    W. Reimann, C. Wells, R. Johnson, R. B. Thompson

Institutional Issues in NDE
    R. Thomson, D. Thompson, R. Anderson, D. Ballard,
    E. Criscuolo, G. Darcy, P. Packman, D. Waidelich,
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WORKSHOP ON FATIGUE CRACK GROWTH

B. Budiansky, D. C. Drucker
J. W. Hutchinson, J. R. Rice

## SUMMARY

Some aspects of fatigue crack growth were discussed at
the July 1976 session of the ARPA Materials Research Council.

A focal point of the meeting was the assessment of
crack surface closure as a basis for prediction of crack growth
under general oscillatory loading histories.  In addition,
fractographic studies, microstructural effects, and environ-
mental influences on crack growth were discussed.  The paper
attempts to identify critical topics for further research.
These relate to the experimental study of closure effects, to
the development of predictive crack growth models at the macro-
scopic level, and to the more detailed understanding of micro-
structural and environmental influences on the crack growth
mechanism.

MEETING ON FATIGUE CRACK GROWTH

July 7-9, 1976

AGENDA

P. C. Paris - Continuum mechanics aspects of fatigue crack
        propagation.

R. M. Pelloux - Relationships between Fractography and
        Microstructure.

J. P. Gallagher - Air Force crack propagation problems and
        needs.

W. Elber - Comparative discussion of methods of closure
        observation.

Discussion by D. M. Corbly and O. Buck (ultrasonics),
W. Reimann (interferometric), G. R. Chanani and R. P. Wei
(electric potential, bridging strain gauge), P. C. Paris
(elastic unloading compliance), and others as appropriate
on closure observations and relevance to mechanisms and/or
models of fatigue.

R. O. Ritchie - Influence of superposed static fracture
        mechanisms on fatigue.

R. P. Wei - General environmental and temperature effects.

O. Buck - Environmental effects on closure and fracture mode.

Discussion by G. R. Chanani (fractographic features associated
with overloads), A. W. Thompson (effect of microstructure in
Ti alloys).

J. W. Hutchinson - Closure effects predicted from Dugdale/BCS
        crack models.

W. Elber - Summary of J. Newman finite-element predictions
        of crack surface closure effects.

H. Dill - Spectrum crack growth prediction.

A. J. McEvily - Modified COD model.

Discussion: Fatigue detection by NDE, modeling, crack growth
prediction.

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# MEETING ON EPITAXY

N. Bloembergen
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## SUMMARY

Members of MRC and a group of experts from both the industrial and the university communities met to discuss the state of the art in epitaxial growth of crystalline layers and the variety of applications which depend on them. It was hoped that the meeting would be able to identify and pinpoint serious problem areas where additional work may be required.

The main topics discussed at the meeting were:

1. The various techniques used in epitaxial growth-primarily liquid (LPE) and vapor phase (VPE) epitaxy and the recently developed technique of molecular beam epitaxy (MBE).

2. The use of epitaxially grown films in the fabrication of a variety of electronic and electro-optic devices, especially CW injection lasers, light emitting diodes, photodetectors for near visible and infrared applications, impatt diodes and field effect transistors, integrated optics, and magnetic bubbles for computer memories.

3. The intriguing possibility of crystal engineering by MBE which makes it possible to grow new crystals with controlled periodicities.

It became clear from the meeting that epitaxy is playing a key role in a great variety of new technologies of increasing importance to U.S. technology and to DoD. A good example is the GaAs-GaAℓAs double heterostructure injection laser which is developed intensely in this country and abroad primarily for powering optical fiber communication links.

The meeting convinced us that due to the combined incentive of commercial and military application and of government support the epitaxial technology is pursued vigorously in the U.S. A few areas, however, were identified where additional effort could play an important role in advancing the technology. These are:

1. The development of U.S. sources for high grade InP crystals is recommended. This material is the starting point for growing epitaxial GaInAsP lasers oscillating near 1.25μm a region where the disperison and loss characteristics of silica based optical fibers are optimum.

2. Development of ternary crystals as substrate sources is recommended. All of today's epitaxial technology is based on starting from binary substrates (GaAs, InP, CdTe, etc.) which places a limit on the flexibility and choice of materials available to device designs.

3. Support of research on the use of organo-metallic compounds in vapor phase epitaxy (VPE) is recommended. VPE techniques will be important in large scale fabrication of epitaxial structures. Present VPE techniques cannot handle reactive

elements such as A$\ell$ and Sb.  Preliminary work in the U.S. and
in Japan indicates that VPE using organo-metallic compounds
(such as A$\ell$$(C_2H_5)_3$), can overcome this problem.  It will also
be important to develop a supply of high purity organo-metallic
reagents.

4.  Studies in academic institutions on the detailed
_kinetics_ of epitaxial growth are recommended.  While the thermo-
dynamic properties are in general, sufficiently well known,
basic knowledge on diffusion rates growth habits, sticking coef-
ficients and non-equilibrium growth is inadequate for the systems
of III-V and II-VI compounds.  The question whether ternary
crystals could provide high grade crystals for use as substrates
should be addressed.

5.  Vapor phase and MBE techniques for InP based systems
should be explored.  Particular attention should be given to
the causes of the generally poorer device performance resulting
from these techniques, compared to LPE.

6.  The garnet epitaxy technology for magnetic bubble
materials appears to be further developed than that of the
compound semiconductors.  It will be important to determine if
this is an inherent property of the different material system,
and if the techniques of a high degree of supercooling and
liquid motion be successfully transferred to III-V and II-VI
systems.

MEETING ON EPITAXY

July 12, 13, 1976

A. Yariv - Introduction

M. Panish - III-V Liquid Phase Epitaxy - From Phase Diagrams to
      to Devices

A. J. Strauss - Liquid Phase Epitaxial Growth of Lattice Matched
      GaInAsP-InP for 1→1.3μm Double Heterostructure Laser

P. Vohl - Vapor Phase Epitaxial Growth of $Hg_{1-x}Cd_xte$ $(0 \leq x \leq 1)$

J. M. Walpole - Epitaxial Growth of $Pb_{1-x}Sn_xTe$

A. Cho - Preparation and Properties of GaAs Devices by Molecular
      Beam Epitaxy

S. Kamath - Infinite Melt Liquid Phase Epitaxy of GaAs and GaAlAs
      for Device Applications

I. Samid, P. Yeh and A. Yariv - Embedded Epitaxy;
      Distributed Feedback and Distributed Bragg Mirror
      Lasers Using LPE Grown GaAs-GaAlAs Structures;
      Optical Properties and Phenomena in Stratified Media

J. Stringfellow - VPE Growth of III-V Materials for Microwave
      Applications

A. Gossard - Coupled Quantum Wells and Alternation Monolayers
      of GaAs-AlAs Structures

J. S. Harris - Liquid Phase Epitaxy Growth of Ternary Alloys
      for Heterojunction Infrared Devices (solar cells and
      photocathodes)

R. Burmeister - Liquid Phase Epitaxial Growth of Magnetic Garnets

Informal Discussion

MEETING ON EPITAXY

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HIGHLIGHTS OF SESSIONS
ON RAPIDLY SOLIDIFIED POWDERS AND RELATED TECHNOLOGY

E. E. Hucke, J. P. Hirth and M. Cohen

The following highlights emerged from the presentations
and discussions on "Rapidly Solidified Powders and Related
Technology." A more explicit summary of these sessions will be
given in the Final Report.

1. It is evident that scientific and technological ideas
concerning rapidly solidified powders and their products are
multiplying in excitement and potential.

2. Further reduction in droplet size appears to be the
most effective way to achieve still faster solidification rates,
($>10^6$ °C/sec); the capability of forced convection in attaining
even greater cooling rates requires more careful definition,
particularly since the processing of fine powders becomes much
more difficult with decreasing particle size.

3. There are new indications that the progressive decrease
in dendritic-arm spacing with increasing solidification rate is
interceded by spontaneous nucleation in the supercooled liquid.
This is a very significant phenomenon because:

a. The microcrystallites or cells thus formed have a
chance to grow just by atom-by-atom jumping across the liquid/

solid interface without compositional partitioning between the liquid and solid phases. Thus, in the limiting case, the micro-crystallites will have exactly the same composition as the liquid, and the resulting grain boundaries can be unusually clean.

b. This prospect shows that it is important to strive for still faster cooling rates or, at least, solidification conditions in which the thermal gradients are large compared to the solid-front growth rate (i.e., without any long-range diffusion).

c. In this new regime, supercooling and nucleation phenomena will play a critical role in the size of the micro-crystallites, possibly reaching down to 10-100A.

d. In the light of these factors, the tolerance for impurities as well as for new alloy compositions can be sharply enhanced; indeed, it may well turn out that a quantum-step improvement in properties can be obtained in these highly-super-cooled, nondendritic structures.

4. Skin-melting of bulk alloys by high-intensity laser-beam heating, together with conductive quenching by the metallic substrate, provides an excellent research tool for producing and studying the above-type of highly supercooled, nondendritic solidification and its competition with dendritic solidification. The inhibition of secondary-phase precipitation on solidification as well as the kinetics and morphology of the precipitation on reheating can also be investigated via this technique, comparing both dendritic and nondendritic structures in the skin-melted zone.

5. Consideration should be given to model alloy systems (such as Pd-Si and Pd-Si-Cu) which, even at conveniently accessible cooling rates applied to a given composition, will exhibit the complete range of processes from dendritic segregation to microcrystalline solidification to amorphous-glass formation.

6. It appears that an electrostatic field tends (a) to stabilize a stream of liquid metal against break-up into droplets, and (b) to damp out oscillations once the droplets are formed. These phenomena should be examined as to origin and possible application to atomization processes.

7. Particular attention should now be given to the powder-consolidation steps and their role in the resulting structure/property relationships. Very little systematic information is available on what happens to the grain size, dendritic structure, and secondary-phase morphology as a function of the processing and heat-treatment variables. These interactions also point up the need (and opportunity) to optimize compositions and treatments in order to take full advantage of the small-particle approach to materials technology.

8. The wide-scale exploitation of rapidly-solidified powder processing will require multi-faceted structure/property research programs on numerous alloy systems. To that end, there is urgent need for flexible, small-lot (¼ to 10 lbs.) powder-making facilities which will permit the detailed study of compositional and structural variables. The availability of such equipment will probably do as much as anything to expand the understanding and

applicability of the resulting materials.

9. Although glassy-metal powders can be produced in some alloy systems, it is still not known whether these powders can be consolidated without degradation of the glassy state. Such experiments might be tried on the Pd-Si and Pd-Si-Cu prototype alloys mentioned in Item 5.

10. Results to date on the powder-processed intermetallics TiAl and $Ti_3Al$ look encouraging; substantial progress has been made during the past year toward achieving some ductility and good fatigue strength along with noteworthy creep resistance.

11. There is increasing evidence that powder processed aluminum alloys exhibit improved resistance to stress-corrosion cracking and to corrosion fatigue, compared to the conventional wrought alloys. This finding has major implications from the standpoint of extending the mechanically-useful range of high-performance materials in typical environments.

12. A promising approach to the ultrasonic nondestructive testing of powder-processed bodies with curved surfaces has been described, based on the use of appropriately-shaped adapters between the transducer and the curved surface.

13. It appears that, in order to take advantage of the expected 100°F improvement in operating temperature for powder-processed jet-engine turbine blades, the development of a protective coating for the state-of-the-art superalloys will become mandatory.

14. Fe-Al-Si alloys look attractive for reasons of special

magnetic properties as well as oxidation and corrosion resistance,
without requiring any potentially strategic metals.  However, the
development of such alloys has been blocked by brittleness problems,
which may now be circumvented by powder processing.  This means
that the stable and metastable phase relationships in the ternary
Fe-Al-Si system should now be roughed out by computational methods.

15.  There are good prospects for substantial advances in
titanium alloy formability and properties through the RSP approach.
However, less expensive methods are needed for producing high
quality titanium powders.

SMALL-PARTICLE PHENOMENA AND TECHNOLOGIES MEETING

July 14-15, 1976

First Session - Morris Cohen, Chairman

  E. C. van Reuth - ARPA Program in Small-Particle
         Processing

  *Alan Lawley - Overview of Advanced Powder-Making
        Processes; Fundamentals of Droplet
        Formation

  *M. C. Flemings - Theory of Dendritic Solidification
         During Very Rapid Cooling

  **J. B. Moore and A. R. Cox - Progress in the P&W Rapid
          Solidification Program

Second Session - E. E. Hucke, Chairman

  *N. G. Grant - Special Methods of Achieving Rapid
        Solidification in Fine Particles

  E. J. Dulis - Inert Gas Atomization and Shape
        Consolidation of Commercial Alloys

  *O. D. Sherby - Fundamentals of Superplasticity;
        Extension to Refractory Metals

  *A. G. Evans - Prospects for Attaining Superplasticity
        in Intermetallic and Ceramic Materials

Third Session - J. P. Hirth, Chairman

  *Larry Kaufman - Calculation of Metastable Phase
        Relationships

  R. E. Maringer - Survey of Microcrystalline - and
        Amorphous - Metal Technologies

 ***Five-minute presentations on new ideas relative to
 processing, structural control, novel properties,
 and applications; preparation of brief memoranda

Fourth Session - Morris Cohen, Chairman

  Identification of important research opportunities
  and potential applications

  Recommendations to ARPA

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SUMMARY OF THE CONFERENCE
ON THE STRENGTH OF OPTICAL FIBERS

A. G. Evans

The intent of this meeting was to discuss the fracture
of large lengths (∿1km) of optical fibers, in order to identify
methods for assessing the structural reliability of these fibers
in a variety of applications.

A presentation of the potential Navy utilization of
optical fibers by G. A. Wilkins of the Naval Undersea Center,
indicated that cable design considerations require that the
fiber be able to withstand relatively long time axial tensile
stresses of at least 100 Ksi and larger localized tensile stresses
(up to 500 Ksi) induced by fiber bending.

It has been well established that optical fibers in short
lengths (∿1m) are capable of withstanding short time axial tensile
stress in excess of 500 Ksi. However, the statistical nature of
the fiber fracture process and the occurrence of slow crack growth
generally results in a much lower long term strength capabilities
when the fibers are fabricated in very large lengths. The long
time structural reliability of long fibers then requires an under-
standing of the time dependence and statistical character of the
fracture strength, the development of techniques that eliminate
the fibers at the low strength extreme of the distribution and,

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if possible, the utilization of fiber strengthening processes. Each of these issues was addressed by a series of four speakers.

The time dependence of fracture strength was discussed by R. H. Doremus. He emphasized the use of delayed failure data on fibers to determine empirical relations (between the failure time and the normalized stress) that provide a good description of the data over the widest possible range of stress. The rationale being that the use of such relations should enhance the confidence in the extrapolation of test data to large times.

The statistical aspects of fiber fracture were described by A. G. Evans. He indicated how recently developed statistical analyses could be used to characterize basic strength distributions from tensile data on relatively small samples, and then those distributions might be used to predict the strength of much larger samples in the presence of both axial strains and bending moments. He also discussed the role of strength distribution analysis for identifying the source of most deleterious flaws.

The strengthening of fibers by the development of surface compressive stress was discussed by P. Macedo. He showed how compressive surface zones can be tailored by utilizing a molecular shifting process and demonstrated the development of 20 Ksi stresses. He also indicated that much larger stresses (>100 Ksi) might be developed by depressing the glass transition temperature of the inner zone relative to the outer zone. Such a strengthening process would be invaluable if the internal defects of the fiber can be removed by more diligent fabrication controls.

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The development of techniques for assessing the structural reliability of fibers was addressed by J. E. Ritter. He emphasized the use of proof testing, but cautioned that the effectiveness of the proof test is strongly dependent on the proof conditions when slow crack growth does not occur; and one such possibility for the fiber is to insure that the proof stress is only applied at temperatures of approximately 100°C. Alternatively, if proof testing has to be conducted at standard room temperature conditions, the deleterious effects of the slow crack growth that occurs while unloading from the proof stress must be taken into account. These effects are not readily derived from available theory and Ritter. proposed the use of laboratory scale testing to identify the cost effective proof cycle.

STRONG OPTICAL FIBERS

July 21, 22, 1976

## AGENDA

G. Wilkins - Navy Requirements for Strong Optical Fibers

R. H. Doremus - Delayed Failure of Glass

J. E. Ritter - Engineering Design and Fatigue Failure of
     Fused Silica Fibers

A. G. Evans - Failure Statistics

D. Kalish - Fatigue Failure in Optical Fibers

Discussions

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CONFERENCE ON METALLIC GLASSES

J. J. Gilman

SUMMARY

To review the present state of knowledge about metallic
glasses, a brief conference was held during the annual meeting of
the Materials Research Council.  This conference had the purposes
of informing interested members of the MRC about metallic glasses,
and of identifying the research approaches toward the study of
these materials that might be most fruitful in generating fresh
understanding.

Some of the questions that arose during the conference
on structure, mechanical behavior, corrosion resistance electrical
properties and the magnetic properties were addressed and suggestions
were made for finding the answer.

METALLIC GLASSES

July 19, 20, 1976


<u>AGENDA</u>

J. Gilman - A Technological Overview

D. Turnbull - Genesis and Structure

R. Hasegawa - Electrical Properties

H. Ehrenreich - Round Table Discussion

L. David - Mechanical Behavior

R. Staehle - Corrosion Resistance

C. Graham - Magnetic Behavior

J. Hirth - Round Table Discussion


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The following pages list abstracts of memoranda, position papers and technical papers that were developed at the 1976 Materials Research Conference. Most of these, as technical papers, will appear in the Final Report of the meeting to be published before the termination of the current contract.

A listing of these is as follows:

Metallic Glass Structures - J. J. Gilman
On the Mechanism of Shear of an Amorphous Metal - J. P. Hirth
A New Approach to Radial Distribution Functions of Glassy
    Metals - H. Reiss and G. H. Vineyard
Electrical Properties and Metastability of Metallic Glasses -
    H. Ehrenreich
Prospects for Improved Flaw Detection by Acoustic Emission -
    F. A. McClintock and G. S. Kino
Prospects for NDE of Powdered Metals - G. S. Kino
Interpretation of Ultrasonic Scattering Theory for Analysis
    and Design of Flaw Detection Experiments - J. E. Gubernatis,
    J. A. Krumhansl and R. M. Thomson
Experimental Characterization of Defects with Elastic Waves -
    L. Adler, G. S. Kino, R. B. Thomson, B. R. Tittman
Variational Techniques for Scattering and Other Problems -
    G. S. Kino
Discrete Model for Elastic Wave Scattering by Defects in
    Elastic Materials - E. W. Montroll
Molecular Dipolar Pyroelectricity - W. H. Flygare
The Use of Bubble Domain Materials for Submillimeter Wave
    Magnetic Devices - P. L. Richards
Heating Effects in High-Frequency Metallic Josephson Devices:
    Voltage Limit, Bolometric Mixing, and Noise - M. Tinkham
Mechanistic Limitations on the Speed of Response of Electro-
    chromic Optical Devices - R. A. Huggins
Fundamental Limitations on Performance of Pyroelectric Vidicon
    Detectors - M. Tinkham and A. Yariv
Closure Analysis in Fatigue Crack Growth - B. Budiansky,
    J. W. Hutchinson, J. R. Rice
Dynamic Elastic Crack Tip Stresses and Displacements for
    Fracture Criteria - F. A. McClintock
Computational Needs for Predicting Plane Strain Fracture -
    F. A. McClintock
Fatigue Crack Growth - P. C. Paris
On the Ratio of Tensile Strength to Modulus of Rupture of
    Ceramics - D. C. Drucker
High Strength Optical Fiber - R. L. Coble
High Strength Optical Fiber - A. G. Evans, F. A. McClintock,
    R. L. Coble

Structural Reliability of Optical Fibers - A. G. Evans and
    F. A. McClintock
Ultrasonic Flaw Detection in Ceramic Turbine Components -
    G. S. Kino and A. G. Evans
Prospects for Superplasticity in Ceramics - A. G. Evans and
    R. L. Coble
Ceramic Turbine Program - R. L. Coble
Fracture Mechanics and the Static Fatigue of Strong Silica
    Fibers - D. C. Drucker
Thermal Stability of CFX in Fluorine - P. Kamarchik and J. L.
    Margrave
Reactions of Li Atoms in Low Temperature Matrices - C. Krishnan,
    P. Kamarchik, P. Meier, R. Hauge and J. L. Margrave
ESCA Studies of Fluorinated PVC and CFX - G. Parks and J. L.
    Margrave
Chlorofluorocarbon Update, 1976 - J. L. Margrave
Solid Sources of Elemental Fluorine. I. Thermal Stabilities of
    Solid Perfluorides and Superfluorides - J. L. Margrave
Solid Sources of Elemental Fluorine. II. Thermal Stabilities
    of Ternary Fluorides - J. L. Margrave
Very Rapid Quenching with Thermal Spikes - G. H. Vineyard
Nucleation, Undercooling and Homogeneous Structures in Rapidly
    Solidified Powders - J. P. Hirth
Curvature Effects in the Thermodynamics of Multicomponent Systems:
    Possible Effect on Dendrite Spacing in Rapidly Cooled Small
    Liquid Metal Drops - H. Reiss
Rapid-Solidification Processing (RSP) of Thermoelastic Alloys -
    M. Cohen
A Key Bottleneck in the Exploitation of Rapid-Solidification
    Processing (RSP) - M. Cohen
Comments on Alternative Methods that Might Be Used to Prepare
    Superhomogeneous-Fine Particles of Metals - R. A. Huggins
Small Particle Technology - R. L. Coble
Theory of Dendrite Solidification During Very Rapid Cooling -
    M. C. Flemings
Pressure in a Spherical Cavity or On a Solid Sphere is Limited
    by Instability - D. C. Drucker
A Fluid Thermal Switch - H. Reiss
Tight Binding Theory of Metallic Adhesion - W. Kohn and R. Gomer
Effect of Electrolyte on Dipole Layer Potentials at a Liquid-
    Solid or Liquid-Air Interface - R. Gomer and H. Reiss
A Mechanism for Liquid Phase Epitaxial Growth of Nonequilibrium
    Compositions Producing a Coherent Interface - J. P. Hirth
    and G. B. Stringfellow

# METALLIC GLASS STRUCTURES

J. J. Gilman

## ABSTRACT

A model for the structures of transition metal-metalloid liquids and the glasses that derive from them is proposed. Existing models are based on dense-random-packing of the metal atoms with the interstices filled by metalloid atoms. The proposed model consists of the dense random packing of specific metal-metalloid clusters immersed in a sea of conduction electrons. It is believed that such a model can better explain: the composition of the eutectic liquid; the relative stability of the liquid; the viscosity minimum at the eutectic composition; and other physical properties.

# ON THE MECHANISM OF SHEAR OF AN AMORPHOUS METAL

J. P. Hirth

## ABSTRACT

Several mechanisms have been proposed for the shear
flow of metallic glasses.  These models are shown to give ex-
plicit predictions of both the flow stress and the strength-
differential effect where the flow stress varies with the
total external stress tensor.  Comparison of results for these
quantities show that the best overall correlation is with a
dislocation-type flow model proposed by Gilman.  A complete
rationalization of data, however, requires a contribution of
a plastic-type dissipative term to the flow resistance.

A NEW APPROACH TO RADIAL DISTRIBUTION
FUNCTIONS OF GLASSY METALS

H. Reiss and G. H. Vineyard

## ABSTRACT

We suggest a novel way of writing approximate equations
which determine the radial distribution functions of multi-
component amorphous systems, including their time dependence
in non-equilibrium situations.  Applications to the structure
of glassy metals are being worked out.

ELECTRICAL PROPERTIES AND METASTABILITY OF METALLIC GLASSES

H. Ehrenreich

## ABSTRACT

The electrical properties and the metastability of
metallic glasses, and their relationship is discussed on the
basis of a "frozen liquid" model with a view of exploring the
general applicability of that model.  Several questions con-
cerning the transport theory of metallic liquids are for the
most part resolved.  These are:

1.  The applicability of a theory based on independent
and strong scatterers (e.g., the transition metal constituents)
whose coordination is specified by the radial distribution
function.

2.  The long standing puzzle concerning the effective
valence $Z_{eff}$ for transition metal liquids which falls in the
range $1 < Z_{eff} < 2$ independently of the liquid under consideration.

3.  The role of the metalloid constituent in electronic
transport.  Recent speculations by Tauc and Nagel concerning
the metastability of metallic glasses are examined using the
same viewpoint.  These considerations are shown to be consis-
tent with those concerning the electrical properties in
accounting for the negative temperature coefficient of the

resistivity $\rho$ observed in many metallic glasses and why this
type of behavior is found in glasses having large $\rho$, whereas
for intermediate values $\rho$ is either temperature independent
or increases with temperature.

PROSPECTS FOR IMPROVED FLAW DETECTION BY ACOUSTIC EMISSION

F. A. McClintock and G. S. Kino

## ABSTRACT

A brief review of increasing needs for flaw detection, the coming use of finer grained materials, and developments in transducers and signal processing resulting from the current work on ultrasonic inspection are all factors indicating bright promise for improvements in flaw detection by acoustic emission, especially by distinguishing between shear and dilatational sources.

# PROSPECTS FOR NDE OF POWDERED METALS

G. S. Kino

## ABSTRACT

A discussion of possible NDE techniques for cast powdered metal structure is given. It is concluded that contacting of curved surface using a mating curved part should not provide a major problem. Detection of small flaws in the 10-50μm size range and comparable to the grain size should be very difficult at distances more than a few millimeters from the surface. The use of focused transducers could help in this respect. Surface waves could be used to detect small flaws near the surface of the order of $\lambda/4$ deep and $\lambda$ in diameter where $\lambda$ is the acoustic wavelength. Initially measurements of attenuation in these new materials must be carried out before good estimates of the resolution capabilities of NDE can be made.

INTERPRETATION OF ULTRASONIC SCATTERING THEORY
FOR ANALYSIS AND DESIGN OF FLAW DETECTION EXPERIMENTS

I.   LONG WAVE LIMIT

J. E. Gubernatis, J. A. Krumhansl, R. M. Thomson

## SUMMARY

Recently[1] it has been shown that the results of the
general theory of ultrasonic scattering, in the far field region,
can be compactly represented by a vector $\underline{f}$.  The experimental
dependence on incident mode, scattering angle change in proper-
ties, and shape can be systemized thereby.  In the long wave
limit $\underline{f}$ may be determined exactly, and significant features of
the flaw are to be found therein.  We discuss this case for both
volume flaws and flat cracks.  Comparison is made with some of
the results of the Born (Rayleigh-Gans) approximation[2] which has
been compared to experiment in some cases.[3]  The high frequency
limit will be discussed elsewhere.

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[1] J. E. Gubernatis, E. Domany, J. A. Krumhansl (to be published).
[2] J. E. Gubernatis, E. Domany, J. A. Krumhansl and M. Huberman,
 Report #2654, Cornell Materials Science Center, also listed
 as ERDA #C00-3161-42.
[3] B. Thompson, B. Tittman: Rockwell Report

# EXPERIMENTAL CHARACTERIZATION OF DEFECTS
## WITH ELASTIC WAVES

L. Adler, G. S. Kino, R. B. Thompson, B. R. Tittman

## SUMMARY

Experimental limitations on the information available
in an ultrasonic scattering experiment are summarized.  Included
are effects due to component geometry, material attenuation,
critical flaw sizes, and wave polarizations.  Within the experi-
mentally accessible regime, the ability of existing scattering
models to describe measurement regions where further work is
needed are identified.  Needs and some approaches towards the
inverse problem, wherein defeat characteristics are estimated
from measured data, are emphasized.

VARIATIONAL TECHNIQUES FOR SCATTERING
AND OTHER PROBLEMS

G. S. Kino

## ABSTRACT

The reaction principle of electro-magnetic theory has
been used to develop new variational techniques for acoustic
wave problems. This has enabled us to obtain relations similar
to those of Kohn and Krumhansl, and to Nemat-Nasser for Eigen
value problems.

By using this reaction principle we have derived a new
type of formalism for scattering of acoustic waves from flaws
in materials. The great advantage of this scattering formalism
is that it makes it very clear which stress terms and displace-
ment terms contribute to the scattering. It does not require
the direct use of a Green's function technique. By simplifying
the mathematics, following established principles, we can reduce
the formula to a Born scattering theory, and have used it to
obtain a scattering formula for the scattering of Rayleigh wave
from a cylindrical hole drilled perpendicular to the surface of
a metal. This formula, in the range where it should be valid
appears to be in reasonable agreement with experimental results
obtained by Viktorov.

We have then gone on to use the reaction principle to derive general variational formulae for scattering from arbitrary defects. These formulae are complicated. So it remains to be seen how useful they will be in their quantitative application to practical problems. However, they may be extremely useful for obtaining a qualitative feel for scattering effects.

# DISCRETE MODEL FOR ELASTIC WAVE SCATTERING
## BY DEFECTS IN ELASTIC MATERIALS

E. W. Montroll

## ABSTRACT

The development of ultrasonic flaw detection methods requires mathematical formulae for scattering of acoustical waves by the flaws in the material being examined. It is well known that the application of traditional scattering theory to scattering by defects has certain limitations. If one requires accurate expressions in the case in which the scattering center is characterized by propagation parameters far different from the normal materials, one is restricted to certain geometrical shapes of the scatterer (spheres, ellipsoids, and cylinders) for which it is possible to find a coordinate system in which the wave equation is separable. While the Rayleigh-Gans-Born approximation is applicable for any shape, it is accurate only in the limit in which the scatterer is acoustically very similar to the normal material and has dimensions which are not large compared with the acoustical wavelength.

We have developed a form of scattering theory from which computer algorithms can be prepared which yield scattering cross sections valid for unusual shaped scatterers and for scattering centers whose acoustical characteristics are far different from those of the normal material.

# MOLECULAR DIPOLAR PYROELECTRICITY

W. H. Flygare

## ABSTRACT

The polarization of a liquid (or solution) of cylin-
drically symmetric dipolar molecules is calculated according
to the Onsager theory of electric moments of molecules in
liquids. Then, assuming the liquid structure can be rapidly
solidified (fast freezing, or matrix technique) in the pres-
ence of the electric field, the polarization is frozen in.
The pyroelectric effect is then estimated on the basis of the
temperature dependence of the polarization. The molecular
model for the temperature dependence involves the fluctuation
in orientation of the cylindrically symmetric molecule in a
cylindrical potential in the solid. Quite large pyroelectric
coefficients are estimated for simple dipolar molecules.

# THE USE OF BUBBLE DOMAIN MATERIALS FOR SUBMILLIMETER WAVE MAGNETIC DEVICES

P. L. Richards

## ABSTRACT

Several classes of magnetic materials are considered which may prove useful for submillimeter wave magnetic devices. Progress has been made recently in the preparation of large high quality crystals of two of these classes, the orthoferrites and the garnets, because of their use in bubble domain devices.

The magnetic resonance properties required for these applications include narrow resonance linewidths, and the ability to tune the resonance to the required frequency by means of changes in composition or by a magnetic field of moderate strength. These properties are difficult to achieve simultaneously, but some useful cases may be found among the rare earth substituted orthoferrites and compensated garnets. The S-state antiferro-magnet $M_nF_2$ also has useful properties.

The use of a tuneable magnetic resonance absorption as an order sorter for a submillimeter Fabry Perot interferemeter or as a selective absorber for a thermal submillimeter wave detector is suggested. In this way it should be possible to make a magnetic field tuned spectrometer that is simple, more efficient, has higher throughput, and higher resolution than currently used tuneable submillimeter spectrometers.

# HEATING EFFECTS IN HIGH-FREQUENCY METALLIC JOSEPHSON DEVICES: VOLTAGE LIMIT, BOLOMETRIC MIXING, AND NOISE

M. Tinkham

## ABSTRACT

In this paper, we analyze nonequilibrium effects within a simple heating approximation for the case of metallic Josephson weak links which have a favorable three-dimensional cooling geometry. Our principal conclusions are: (1) The temperature in the center of the junction with voltage V applied is $T_m = [T_b^2 + 3(eV/2\pi k)^2]^{\frac{1}{2}}$ where $T_b$ is the bath temperature, e is the electronic charge, and k is Boltzmann's constant. This $T_m$ can be as high as 70 K in Nb point contacts on a high Josephson step; thus the device noise temperature $T_N \simeq \frac{1}{2}(T_b+T_m)$ can greatly exceed $T_b$. (2) The critical current falls approximately as $e^{-P/P_o}$, where P is the power dissipated in the junction and $P_o$ is typically 10 μW for Al, Sn, Pb, and Nb, but much smaller for $Nb_3Sn$. This leads to a decrease in the amplitude of Josephson steps at high voltages which is in good agreement with data on the best Sn variable-thickness microbridges and Nb point contacts. In a junction of optimized resistance level, the overall maximum voltage at which microwave-induced steps can still exceed the noise is predicted to be proportional to $T_c[\Omega\xi(0)/\rho_o]^{2/7}(\nu_1/T_c)^{1/7}$, where $\Omega$ is the solid angle of the

three-dimensional cooling, $\xi(0)$ is the extrapolated coherence length at T = 0, $\rho_0$ is the residual resistivity of the metal, and $\nu_1$ is the microwave frequency. (3) The thermal response should be fast enough ($\sim\tau_{GL}$) to allow detection (heterodyne or square-law) with bandwidth as large as the energy gap frequency; it is estimated that this bolometric detection effect will dominate true Josephson detection for carrier frequencies above $\sim 3$ THz (i.e., $\lambda \leq 100$ μm) in junctions with resistance 10 $\Omega$ or less.

MECHANISTIC LIMITATIONS ON THE SPEED
OF RESPONSE OF ELECTROCHROMIC OPTICAL DEVICES

R. A. Huggins

## ABSTRACT

Non-volatile electrochromic devices for both analog and
digital information storage and display by means of electrically
controlled changes in optical reflectance or absorption are be-
ing investigated in several laboratories.  Broad absorption
bands in the infrared may also lead to various other types of
applications.

A general description of electrochromic systems is pre-
sented, along with the principles of their operation, and the
range of operating characteristics of present systems.

The physical mechanisms involved in the operation of
these systems are reviewed, and the limitations upon the speed
of response under several sets of limiting conditions calcu-
lated.

Requirements for the active materials in electro-
chromic systems and the possibilities for the development of
all solid systems are reviewed.

# FUNDAMENTAL LIMITATIONS ON PERFORMANCE OF PYROELECTRIC VIDICON DETECTORS

M. Tinkham and A. Yariv

## ABSTRACT

Even if one were given a pyroelectric material with arbitrarily large pyroelectric coefficient and a noiseless readout system, the sensitivity of a pyroelectric vidicon system would be limited by thermodynamic fluctuations. In this paper we first treat this ideal limit, then consider the degree to which practical systems approach it, and finally analyze the potential for improvements. From our analysis we conclude that:

1. The best present pyroelectric vidicons already have sensitivities that are close to the limit set by thermodynamic fluctuations in their retinas. Thus there is probably only limited scope for improved performance by further reduction of amplifier and electron beam noise, although an improved pyroelectric material might reduce the stringency of the amplifier requirements.

2. The only direct route toward better performance is by lowering both the thermal conductance and heat capacity of the retina, essentially by making it thinner. If fabrication can be managed, it appears in principle possible to operate

with a retina as thin as ~1.4μm, with a ~25-fold increase in
signal and ~5-fold increase in fluctuation noise relative to
a 30μm retina.  A 5-fold reduction in minimum detectable
temperature difference would result if such a thin retina
could be used.  The increased responsivity would actually
make amplifier requirements less stringent than in present
devices.

3.    Reticulation of the retina can increase spatial
resolution at the expense of temporal resolution, but only
a proportionate reduction of both heat capacity and thermal
conductance can improve sensitivity without change of response
time.

4.    If much thinner retinas can be developed, it will
be important to devise improved readout schemes which involve
less energy deposition in the retina, in order that the full
potential benefit of reducing the thermal conductance of the
retina can be realized.

# CLOSURE ANALYSIS IN FATIGUE CRACK GROWTH

B. Budiansky, J. W. Hutchinson, J. R. Rice

## ABSTRACT

Experimental studies have indicated that the purely mechanical phenomenon of crack closure may be a significant factor in fatigue crack growth. Plastically stretched asperities left behind an advancing crack tip may cause the crack to close up prior to attainment of the minimum load. During the portion of the load cycle in which the crack tip is closed, it is essentially immune to changing load. A model including crack closure under steady cyclic loading has been formulated where the load, as measured by the stress intensity factor $K$, varies between $K_{max}$ and $K_{min}$. The model is an extension of the Dugdale model and incorporates a residual stretch $\delta_R$ behind the crack tip as shown in Fig. 1. First contact of the surfaces occurs a distance $S_c$ behind the tip at a value $\Delta K_c$ below $K_{max}$. The dependence of these quantities on $\delta_R$, together with that of the reversed plastic zone size at first contact $\omega_c'$, are shown in Fig. 2. Here $\omega_{max}$ and $\delta_{max}$ denote the plastic zone size and crack tip opening displacement at $K_{max}$.

The residual stretch $\delta_R$ is determined uniquely by the requirement for internal consistency that its magnitude be such
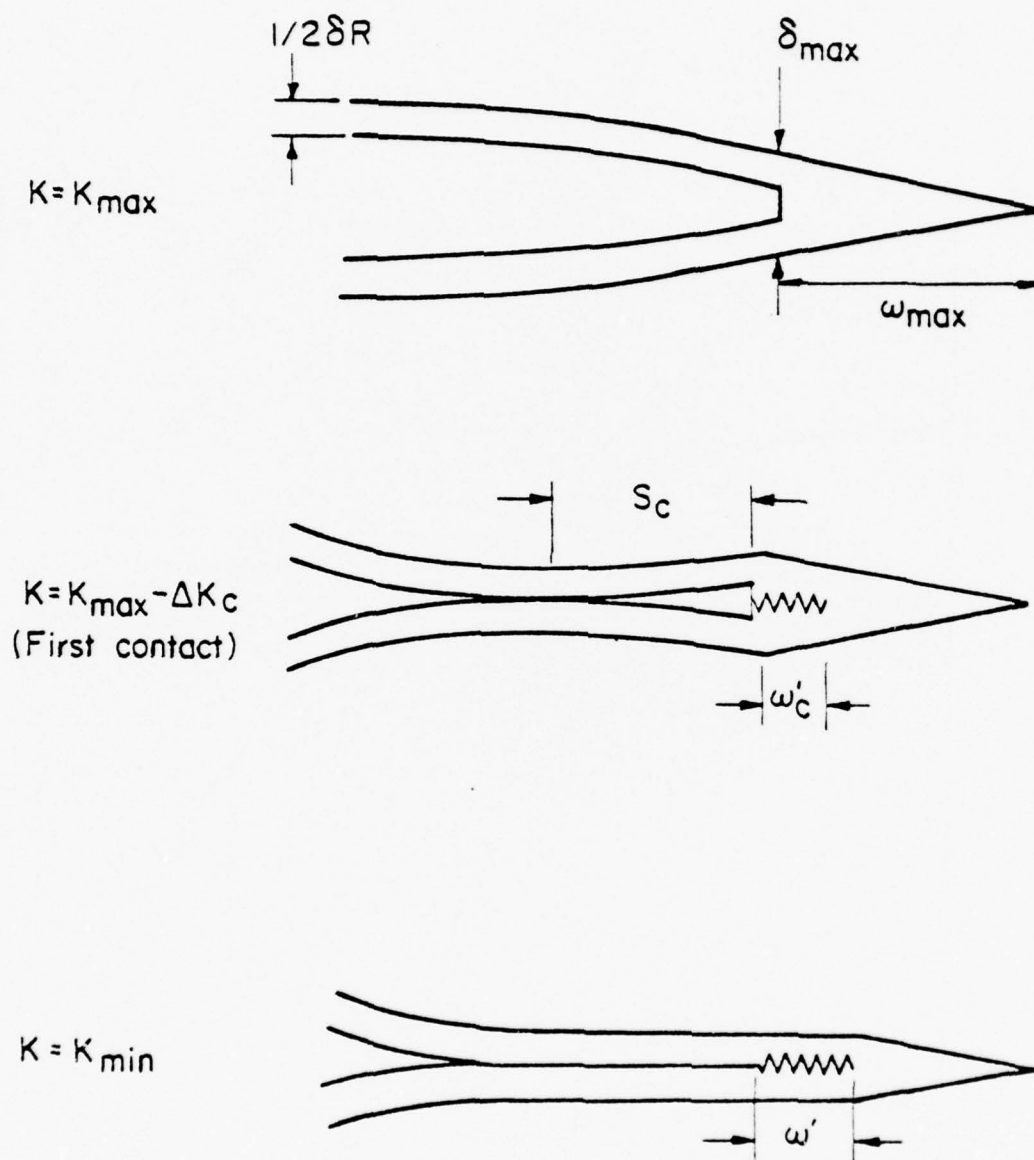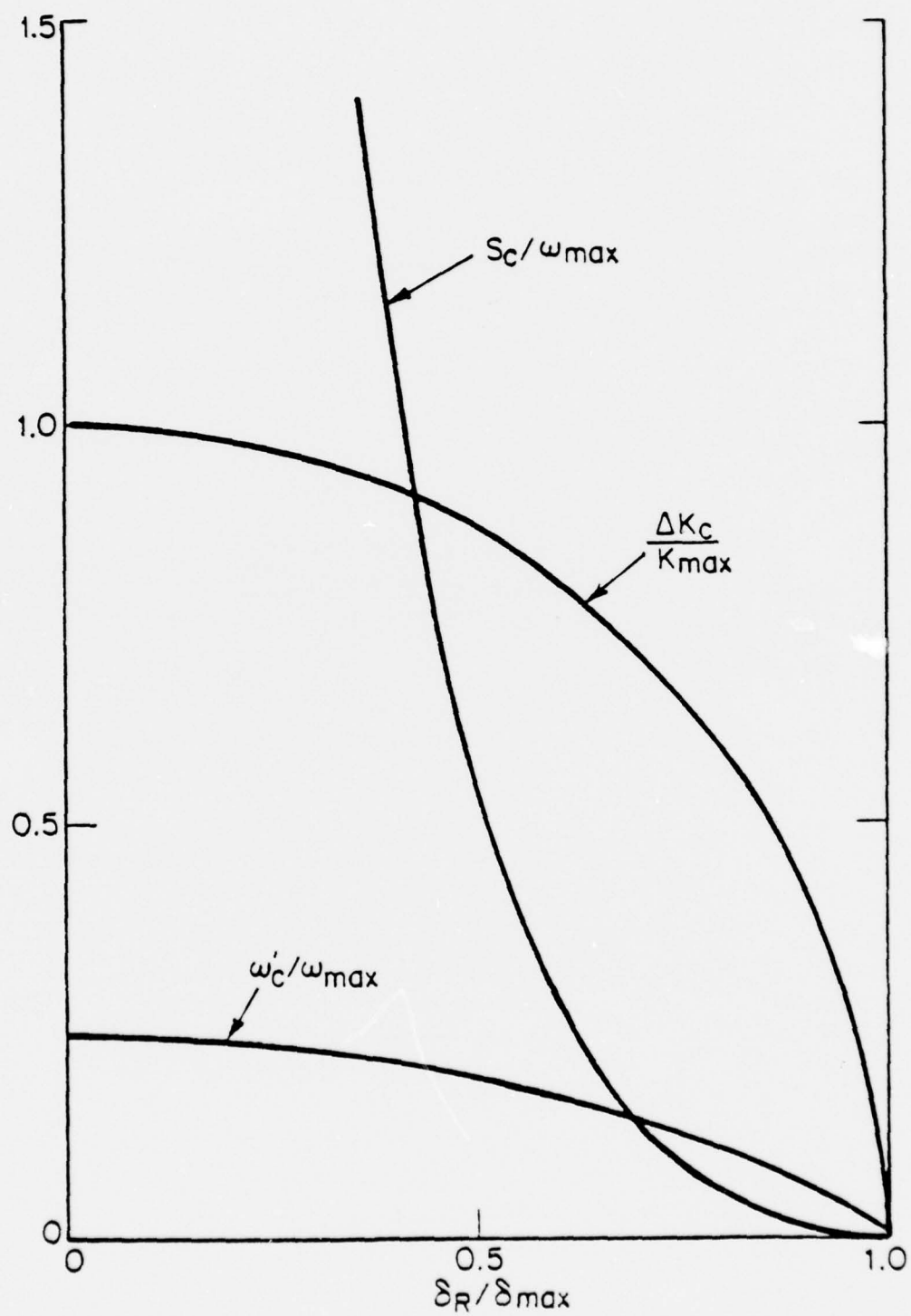
FIGURE 1.

FIGURE 2.

that the surfaces immediately behind the tip are closed at $K_{min}$ with stresses which do not exceed yield in the contact region.

Preliminary estimates have been obtained for some quantities of interest for the case $K_{min} = 0$. We find

$$\delta_R/\delta_{max} = 0.86 \quad , \quad \omega'/\omega_{max} = 0.093$$

where the value of $\omega'$ pertains to $K = K_{min}$ and is less than one half of the corresponding value found when closure is ignored. From Fig. 2 it can be noted that first contact occurs for $\Delta K_c/K_{max} \simeq 0.50$ with an associated reversed plastic zone $\omega_c'/\omega_{max} \simeq 0.07$. Relatively little further reversed plastic deformation takes place after first contact. Thus the effective variation of the stress intensity factor experienced by the material undergoing reversed straining at the tip if $\Delta K_{eff} \simeq 0.50\ K_{max}$ for $K_{min} = 0$, in accord with Elber's experimental findings.

We intend to sharpen the definition of $\Delta K_{eff}$ and then explore the effect of load ratio, $K_{min}/K_{max}$. Extensions to variable amplitude loadings will also be considered.

DYNAMIC ELASTIC CRACK TIP STRESSES AND DISPLACEMENTS
FOR FRACTURE CRITERIA

F. A. McClintock


## ABSTRACT

For dynamic crack growth calculations the fracture
criterion cannot consist solely of the critical stress in an
element, because the critical stress intensity factor would
then depend on element size. Rather, the crack velocity
should be taken to be a function of the dynamic stress singu-
larity. Equations for the necessary stress and displacement
fields are gathered from the literature and plotted to show
the very marked distortion that increases from 10% through a
factor of 2 at speeds of 1/3 to 2/3 of the Rayleigh wave
velocity. The crack openings between elements near the crack
tip can be used with these results to obtain the dynamic stress
singularity, and hence, from test data, the current crack
velocity.

# COMPUTATIONAL NEEDS FOR PREDICTING
## PLANE STRAIN FRACTURE

F. A. McClintock

## ABSTRACT

Numerical solutions in plane strain plasticity are needed to help predict fracture from small, relatively plastic or creep-fatigue types of test specimens; to predict possible improvements in alloy microstructure; and to test semi-empirical fracture criteria. Plane strain is chosen to allow modeling of most of the physical mechanisms of fracture and the effects of triaxiality, because at least some analytical solutions are available, because of the feasibility but high cost of numerical solutions, and because the methods for plane strain can be easily extended to plane stress, but not necessarily conversely.

An outline is presented to help gather information for planning, coordinating, and interpreting such numerical solutions for problems involving fracture under monotonic or repeated loads.

FATIGUE CRACK GROWTH

P. C. Paris

ABSTRACT

A review is given of fatigue crack growth, with par-
ticular reference to the role of crack closure as a basis for
understanding load ratio and overload effects in fatigue.

ON THE RATIO OF TENSILE STRENGTH TO MODULUS
OF RUPTURE OF CERAMICS

D. C. Drucker

## ABSTRACT

A direct tensile test of a brittle material, such as a
ceramic, requires great care in alignment of load and specimen.
Stress concentrations due to fillets and end attachments are
very troublesome.  It is far more convenient to perform a bend
test which offers just a few easily solved problems of support
and load point constraint.  If the material everywhere is
linear elastic to failure the modulus of rupture, Mc/I, is the
tensile strength of the material in the outer region of maximum
stress.  A tensile specimen of the same dimensions as the beam
would be expected to fail at a somewhat lower stress because
the number of flaws of a given size in its surface or volume is
so much greater than in the small region of high tensile stress
in the beam.

The major point to be made here is not to highlight this
well-known statistical effect which currently is taken into
account.  Rather it is to bring out equally well-known effects
that nowadays tend to be ignored although they cause the modulus
of rupture to be an appreciable overestimate of tensile strength.
These include creep, plastic deformation, stable cracking and

and crack growth prior to final fracture. Plasticity or highly nonlinear creep leads to the well-known factor approaching 1.5, found for sintered tungsten carbide, even when so localized at the boundaries of the ceramic particles or grains as to give an apparently linear load-deflection curve to fracture. Extensive stable cracking or much larger creep rates in tension than compression shifts the neutral axis and can give ratios of modulus of rupture to tensile strength as high as 2 or 3 in extreme cases.

# HIGH STRENGTH OPTICAL FIBER

R. L. Coble

## ABSTRACT

For the programs underway, emphasis has been placed on glass fibers and claddings; support of the development of crystalline fiber is warranted because:

1) Crystalline $Al_2O_3$ fiber (1 to 125 mils diameter) has been grown continuously at rates up to 200"/hr (at a net cost that is regarded as competitive with other high modulus reinforcement);

2) The intrinsic attenuation is lower for crystalline fiber;

3) The susceptibility of $Al_2O_3$ to strength degradation due to handling or to static fatigue due to water vapor corrosion is much lower than for silicate based glasses (the average strength achieved in uncoated $Al_2O_3$ fiber after handling was →900 Ksi in a humid atmosphere).

An analysis of cost projections with equipment designed for production (rather than laboratory operation) is needed, and an investigation of purification effects on increased growth rates and reduced attenuation losses is warranted because positive results can be expected for both if this program is pursued. Growth of crystals other than $Al_2O_3$ which are more amenable to the development of graded indices of refraction should also be supported (e.g. $MgAl_2O_4$).

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# HIGH STRENGTH OPTICAL FIBER

A. G. Evans, F. A. McClintock, R. L. Coble

## ABSTRACT

The high strength optical fiber development programs
have in common a lack of agreement between the strength tests
on short fiber and the strength exhibited in long lengths; the
strengths in short lengths being greater than that found in
desired service lengths.  It is not now known whether this dis-
crepancy arises from: 1) inadequate assessment of the low stress
probabilities of failure because of small sample sizes; or 2)
a second flaw population not related to the sources of those
which govern the small sample strengths; or 3) aging effects;
or 4) further damage sources in proof testing, handling, cable
fabrication, or early service testing.  Of this group, positive
approaches toward answers can be made to several of the problem
areas, while the possible entry of unrecognized variables pre-
cludes definitive analysis of the remainder.

1.  State-of-the-art statistical analysis techniques
and test techniques to generate the Weibull parameters are
straightforward for determination of whether the short versus
long length samples' flaw populations are single/bimodal.

2.  Fracture of the longer lengths takes place at low

stress levels such that the specimen does not disintegrate. Both ends of the samples at each break should be collected for fractography; examination of the fracture surfaces to trace to the origin and inspection for inclusions, pores, surface particles, or surface irregularities, and beam probe analysis of the fracture surfaces and origins should reveal whether extraneous matter is responsible for the problem.

3. Aging effects only arise with flaws present, imposed tensile stresses, and a corrosive environment. In this case, the generally unspecified histories of sample handling, storage and cable winding from past data can not be unravelled. However, procedures for these operations can be designed to ameliorate the conditions such as to reduce strength degradation in aging.

4. Other possible damage sources are not specified except for those which might arise in proof testing: stick-slip on the capstans used in continuous testing, and damage due to flaw growth during unloading. Both could be eliminated by 1) making the capstan surface very compliant (tangentially) and 2), proof testing in liquid nitrogen, respectively.

# STRUCTURAL RELIABILITY OF OPTICAL FIBERS

A. G. Evans and F. A. McClintock

## ABSTRACT

When optical fibers are fabricated in very large lengths ($\sim$1 km), a significant proportion of failures are commonly encountered at relatively low stress levels. It is important that these failures either be statistically predictable or be eliminated by proof testing.

Methods for characterizing strength distributions in optical fibers from tensile tests on relatively short fiber lengths are described; and the use of such distributions for predicting failure on long lengths of fiber, subjected to axial strains and localized bending moments, is discussed. Also, the role of strength distributions as the isolation of defect origins is indicated.

The proof testing of optical fibers to truncate the strength distribution at an appropriate strength level is an attractive possibility. However, proof testing in environments that cause significant slow crack growth does not necessarily produce the desired truncation. The key relationships between the proof test cycle and the resultant strength distribution are thus described, to provide a rationale for devising effec-

tive proof cycles. Alternatively, proof testing might be con-
ducted at temperatures, $\leq$ -100°C, where slow crack growth does
not occur. Heat transfer through coated optical fibers has
been evaluated to demonstrate the feasibility of proof testing
at such temperatures.

# ULTRASONIC FLAW DETECTION IN CERAMIC TURBINE COMPONENTS

G. S. Kino and A. G. Evans

## ABSTRACT

Several types of surface and internal defects can be
created in the fabrication of complex ceramic components such
as turbine rotors. Certain of these defects should be amenable
to detection by ultrasonic waves. Hence, short and long term
ultrasonic approaches that might be used to detect such defects
in both the preform and sintered condition are discussed. For
short term requirements, primary emphasis is placed on the
detection of relatively large flaws using existing circuitry in
conjunction with single transducers designed to induce either
surface or bulk waves in the 2 to 20 MHz range. For longer
term problems, the potential of multi-transducer B-scan and
imaging systems for use at frequencies up to $\sim$400 MHz are
explored.

PROSPECTS FOR SUPERPLASTICITY IN CERAMICS

A. G. Evans and R. L. Coble

## ABSTRACT

The deformation characteristics of polycrystalline
ceramics have been examined in order to determine the prospects
for attaining superplasticity. The stress dependence of the
deformation rate ($m$) for most ceramics appears to exhibit a
useful range of temperature and stress wherein plastic stability
($m \sim 1$) should be realized. However, the deformation of typical
ceramic polycrystals (within this regime of stress and tempera-
ture) in the presence of a tensile stress is invariably accom-
panied by the formation of cracks or cavities. Three approaches
have been identified that might limit this crack development;
(a) the use of a multiphase system which forms a large propor-
tion of viscous phase at the deformation temperature, (b) the
application of hydrostatic compression in the forming process,
(c) the design of microstructures that optimize the micro-
structural size, the coefficients of diffusion and the grain
boundary viscosity. The latter approach, which is the most
desirable in terms of both forming facility and material qual-
ity (creep and fracture resistance) after superplastic deform-
ation has been examined in detail, leading to suggestions for
microstructural design studies that might result in tensile
superplasticity.

# CERAMIC TURBINE PROGRAM

R. L. Coble

## ABSTRACT

The Ford ceramic turbine demonstration program will fail unless defects generated in fabrication can be eliminated from all parts or a NDE or early proof test technique can be used to identify parts that are free from defects to be processed through sintering, hub-bonding, spin testing, and finally, engine testing. Improved grinding and cleaning procedures for the powder, and an emphasis on avoidance of contamination in processing are essential to eliminate inclusions larger than the particle size that is basic to the $Si_3N_4$ chemistry. Other fabrication flaws which originate from injection molding may be surveyed in the as-fabricated condition by suspension of the parts in a variable density liquid column or a temperature controlled liquid with a density that matches the as-fabricated parts. These should help to identify the presence of low density regions in the parts that evolve into large fabrication voids upon sintering. Alternatively, spin testing after burn-out of the polymer used for injection molding could also be used to eliminate samples with undesirable fabrication voids from the population.

To assist in the identification of fabrication flaws, fractography should be applied to all samples previously broken (when possible) and also to other finished test samples or components after destructive testing. Binocular optical microscopy with a diffuse light source and scanning electron microscopy, coupled with beam-probe analysis of identifiable inclusions, should be used for tracing back to the sources of extraneous included matter. Otherwise, the shapes and sizes of holes, pores, or cavities and any change in the local grain size or pore distribution near the fracture source in comparison with the average (good?) matrix microstructure should be noted.

FRACTURE MECHANICS AND THE STATIC FATIGUE
OF STRONG SILICA FIBERS

D. C. Drucker

## ABSTRACT

An explanation is proposed to resolve a troublesome
paradox reported by John Ritter.  Fracture mechanics concepts
provide a consistent correlation of the tensile strength of
very strong silica fibers with their time to failure in static
fatigue at lower stress.  Similar consistency is found for
conventional fracture mechanics specimens with purposefully
introduced macrocracks.  The embarrassing paradox arises when
the data obtained from macrocracked specimens is applied to
the fibers; the static fatigue lifetimes as predicted from
their tensile strength are many orders of magnitude too long
and the exponent -N of the stress dependence is -35 instead
of -20.

The explanation offered here is that the very small
surface microcracks or equivalent defects cause the effective
stress intensity factor $K_e$ at the surface of the fracture
mechanics specimen to be appreciably higher than the K for the
macrocrack itself.  Rapid brittle fracture occurs under contin-
ually increasing load when $K_e$, not K, reaches the critical
value of $K_{Ic}$.  However, it is K and not $K_e$ that controls the

slow advance of the macrocrack in the long static fatigue life-
times regime. A hidden or ignored ratio of $K_e/K=2$ would appear
as $(2)^N$ in the expression for time to failure, and give the
consequent enormous overestimate (or order $10^{10}$) of static
fatigue lifetime of the fiber based on its tensile strength.
It also would account for the apparent increase in N, and so
fully reconcile the static fatigue lifetime data from the strong
fibers and the fracture mechanics specimens.

# THERMAL STABILITY OF CFX IN FLUORINE

P. Kamarchik and J. L. Margrave

## ABSTRACT

The thermal decomposition of CFX (carbon monofluoride of variable stoichiometry) has been studied over a range of temperatures in vacuum, in $O_2$, in $N_2$ and in $F_2$. Also, the products of decomposition have been collected and characterized by matrix-isolation spectroscopy. In vacuum or in $N_2$ the decomposition proceeds extensively at 500-600°C to yield mainly $C_2F_4$ (gas) with smaller amounts of $CF_4$(gas), $C_2F_6$(gas) and $C_3F_8$(gas). In the presence of $O_2$, some $COF_2$ is also formed which dissociates to $CO_2$ and $CF_4$.

In the presence of $F_2$, solid CFX decomposes very slowly even at 800°C. It appears that $F_2$ at a level of only 1-2% is sufficient to suppress CFX decomposition. Thus, solid carbon or graphite objects with a CFX protective layer should be useful in the presence of elemental fluorine at temperatures of ∼1000°C.
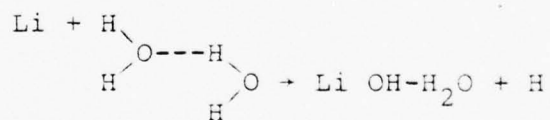
# REACTIONS OF Li ATOMS IN LOW TEMPERATURE MATRICES

C. Krishnan, P. Kamarchik, P. Meier,
R. Hauge and J. L. Margrave

## ABSTRACT

In matrices of Ar, $N_2$, $O_2$, etc., at low temperatures one can observe electron-transfer processes involving Li, Na, K, etc., as electron donors via IR, Raman and ESR spectroscopy. Thus, in the presence of CO one observes $CO^-$, $C_2O_2^-$, and $C_2O_2^=$. This latter ion $(O-C\equiv C-O)^=$ is of considerable potential as a starting material for organic syntheses.

With $H_2O$, $H_3N$ and various amines, one observes partial charge transfer and reactions like

$$Li + \begin{matrix} H \\ \phantom{} \\ H \end{matrix}\!\!\diagdown\!\!\diagup O---\begin{matrix} H \\ \phantom{} \\ H \end{matrix}\!\!\diagdown\!\!\diagup O \rightarrow Li\ OH-H_2O + H$$

With $C_2H_4$, $C_2H_2$ and various $C_2H_3X$ species there is partial charge transfer and, in some cases, halogen abstraction to form LiX and a hydrocarbon radical.

ESCA STUDIES OF FLUORINATED PVC AND CFX

G. Parks and J. L. Margrave

## ABSTRACT

ESCA studies of CFX samples of various stoichiometries have failed to show any evidence for intercalated $F^-$ or $F_2^-$ in the layered structure. Only $-C-F$ and $CF_2$ types of fluorine were identified.

The reaction of $F_2$ with thin films of polyvinyl chloride has been monitored by ESCA. The hydrogens are sucessively replaced and after long fluorination, the polymer is converted to $+C_2F_3Cl+_x$; no chlorine is displaced.

# CHLOROFLUOROCARBON UPDATE, 1976

J. L. Margrave

## ABSTRACT

In order to allow a reliable evaluation of the potential effects of chlorine-containing molecules being introduced by man into the atmosphere there have now been several sampling studies at various levels to establish the concentrations of $CCl_4$, $CCl_2F_2$, $CCl_3F$, HCl, etc., as quantitatively as possible.

There is still evidence for both a natural origin and a natural sink for $CCl_4$. Also, HCl and $CCl_4$ can result from high temperature reactions in fumaroles and volcanos. A new molecule, HCOCl, some ionic clusters and the ClO ion have been studied quantitatively. The importance of carbenes in the upper atmosphere is still unknown.

When the available data are inserted into the ozone layer model calculations, it is still not possible to make definitive statements about the relative effects of natural and anthropogenic chlorine on the ozone layer thickness. As a first iteration, it now appears that "natural" $CCl_4$ and the surprisingly high HCl concentrations in the stratosphere tend to reduce the threat to the ozone layer by anthropogenic chlorine. It is obvious that there is still a lot of unknown chemistry of the atmosphere to be elucidated.
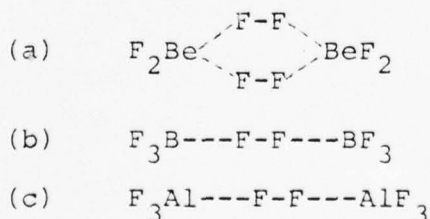
SOLID SOURCES OF ELEMENTAL FLUORINE

I.   THERMAL STABILITIES OF SOLID PERFLUORIDES AND SUPERFLUORIDES

J. L. Margrave

## ABSTRACT

Various possible interactions of elemental fluorine with ionic or covalent fluorides to provide $\dashv$F-F$\vdash$ (perfluoride) or $\dashv$F-F-F$\vdash$ (superfluoride) character are considered from the view-points of thermodynamic cycle and bond energy arguments. Preliminary calculations suggest that ionic solids like $(K^+; F_2^-)$ or $(K^+; F_3^-)$ are likely to be stable enough to serve as practical sources of $F_2$(gas) when heated moderately.

The perfluorination of electron-deficient molecules like $BeF_2$, $BF_3$, $AlF_3$, etc., to yield perfluoro-species is energetically favorable. For example, the following molecules

(a)    $F_2Be\diagdown\begin{smallmatrix}F-F\\F-F\end{smallmatrix}\diagup BeF_2$

(b)    $F_3B\text{---}F\text{-}F\text{---}BF_3$

(c)    $F_3Al\text{---}F\text{-}F\text{---}AlF_3$

are thermodynamically stable and should decompose to yield $F_2$ (gas) at temperatures in the 500-1000°C range.

A perfluoro-bridge between two HF molecules is also energetically and structurally acceptable.

SOLID SOURCES OF ELEMENTAL FLUORINE

II.  THERMAL STABILITIES OF TERNARY FLUORIDES

J. L. Margrave

## ABSTRACT

The interaction of binary fluorides involving an alkali fluoride and the highest oxidation state fluoride of either Group V elements (P, As or Sb) or Group IV elements (Si, Ge, Sn or Pb) leads to two families of ternary compounds:

$MAF_6$ where a = a Group V element and M = a univalent cation

$M_2BF_6$ where B = a Group IV element and M = a univalent cation

the A and B elements have multiple oxidation states and reactions like

$$MAF_6 (solid) = MAF_4 (solid) + F_2 (gas)$$
$$M_2BF_6 (solid) = M_2BF_4 (solid) + F_2 (gas)$$
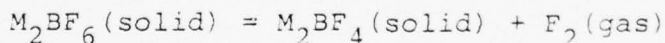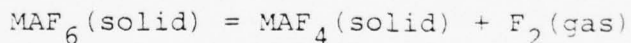
occur according to recent mass spectrometric studies.

Thermodynamic data to evaluate the equilibria quantitatively are only estimated but experimental data show that $KAsF_6$ and $KSbF_6$ do yield appreciable elemental fluorine when heated at 300-500°C.  Also, $M_2SnF_6$, $M_3FeF_6$, etc., can be formed and should yield elemental fluorine when heated.

Solid materials like these should be practical field sources of fluorine for $H_2/F_2$ lasers and an optimum material can be selected on the basis of economic, chemical and engineering criteria.

# VERY RAPID QUENCHING WITH THERMAL SPIKES

G. H. Vineyard

## ABSTRACT

When a heavily ionizing particle such as a fission
fragment passes through matter, a process of rapid heating
followed by rapid cooling occurs in the neighborhood of the
track of the particle.  In radiation damage this effect is
called a thermal spike.  It is suggested here that this process
of very rapid cooling may be of interest as a means of study-
ing the effects of ultra rapid quenching in alloy systems,
and possibly even of processing material.  The process is
examined quantitatively.  For a fission fragment in a metal
of moderate atomic weight such as iron, temperature rises of
more than 500°C are predicted to occur inside a cylinder 200Å
in diameter and quench rates inside this cylinder are calcu-
lated to exceed $10^{12}$ °C/sec.

NUCLEATION, UNDERCOOLING AND HOMOGENEOUS
STRUCTURES IN RAPIDLY SOLIDIFIED POWDERS

J. P. Hirth

## ABSTRACT

The possibility is considered that sufficient under-
cooling of powder particles can be achieved to result in a
microstructure consisting of homogeneous microcrystallites.
A relation is developed for the maximum achievable undercool-
ing for comparison with the undercooling required for such
homogeneous powder.  Sample calculations for the case of mer-
cury, where homogeneous nucleation data are available, show
that it is possible to attain such undercoolings.

From a practical viewpoint, the results show that
effort to achieve even greater rates of cooling would be
worthwhile.  Also, they indicate that in addition to cooling
rate, attention should be directed to decreasing impurities
and other heterogeneities which would tend to cause hetero-
geneous nucleation and prevent the attainment of the maximum
possible undercooling.

CURVATURE EFFECTS IN THE THERMODYNAMICS OF MULTICOMPONENT SYSTEMS:

POSSIBLE EFFECT ON DENDRITE SPACING IN RAPIDLY

COOLED SMALL LIQUID METAL DROPS

H. Reiss

## ABSTRACT

It is shown that the chemical potential of a component
of a small drop, crystal, or crystal dendrite, contains a pre-
viously overlooked term if the drop of crystal is multicomponent.
The new term involves the derivative of the surface tension with
respect to the mole numbers of the component in question, and
becomes negligible for drops or crystals of macroscopic dimensions.
On the other hand, for small systems the equilibrium between the
drop or crystal and the surrounding phase may be severely affected
by the new term.

This can have important implications for the aging of a
precipitate (Ostwald ripening) or for the fine grained dendrite
structures found in rapidly cooled ($10^5$deg/sec) small liquid
metal drops.  Such dendrite structures age by a process similar
to Ostwald ripening.

A model system is introduced in connection with which
illustrative calculations can be, and are, made to demonstrate
the magnitude of the new effect.

# RAPID-SOLIDIFICATION PROCESSING (RSP) OF THERMOELASTIC ALLOYS

M. Cohen

## ABSTRACT

In some alloy systems, the strain energy accompanying the displacements of martensitic transformations on cooling can be accommodated elastically in the alloy, and this becomes available to help drive the reverse transformation on heating. Except for some hysteresis, a thermoelastic balance is set up between the chemical driving force and the stored elastic energy. These thermoelastic systems exhibit rubberlike behavior on loading and unloading because the applied stress shifts the thermoelastic balance; in other words, the operation of martensitic shears on loading and the reverse transformation shears on unloading result in extraordinary stress-strain characteristics for metallic systems.

One of these alloys is Cu-14A$\ell$-3Ni, which is relatively inexpensive and could be commercially feasible, but it suffers from undue brittleness arising from grain boundary precipitates occurring on cooling of the parent phase to room temperature. This undesirable precipitation cannot be inhibited in bulk materials, even by the most rapid quenching, but may well be suppressed or rendered innocuous by RSP methods. If the pre-

cipitation happens to take place during the consolidation step, it is not likely to be intergranular and hence should not cause embrittlement. Another limitation of conventional Cu-Aℓ-Ni alloys is that they are typically coarse grained and do not respond to grain refining treatments. In contrast, the RSP approach should lead to ultrafine grain sizes with beneficial effects on the mechanical properties, and thus provide a superior base for the thermoelastic behavior.

A KEY BOTTLENECK IN THE EXPLOITATION OF
RAPID-SOLIDIFICATION PROCESSING (RSP)

M. Cohen

## ABSTRACT

A case is made for the implementation of flexible, small scale RSP powder making facilities in order to extend and diversify research and development on many materials systems, particularly in the direction of structural control and structure/property relationships.  The availability of such equipment, preferably adaptable to laboratory operation and not necessarily of a single design, is likely to do as much as anything else to expand the understanding and applicability of RSP materials.  Moreover, the full benefit of RSP technology will inevitably require detailed studies of numerous parameters and their optimization, e.g., compositional variables, solidification rates, consolidation steps, and heat treatments.  This type of development will likewise depend on ready access to small quantities of RSP powders.

Under these circumstances, it would be desirable for ARPA to elicit proposals for several types of small lot (1/4-10 lbs.) RSP powder making machines with designated versatility for a range of materials.  These proposals could be aimed at either the design and construction of the equipment in question or at the operation of central facilities for supplying the necessary RSP materials on request.

COMMENTS ON ALTERNATIVE METHODS THAT MIGHT BE USED TO PREPARE
SUPERHOMOGENEOUS-FINE PARTICLES OF METALS

R. A. Huggins

## ABSTRACT

There is certainly greatly increased interest in the
preparation of bulk materials by consolidation of fine particles.
In some cases, fine particles provide superplasticity, and thus
aid densification processes.  In others, microstructural homo-
geniety can be greatly enhanced in a final product fabricated
from particles with fine internal microstructures which resulted
from rapid cooling of small particles from the melt.

This latter point is of special importance, and a great
deal of effort is being expended on techniques for the produc-
tion of fine metallic droplets and their rapid quenching in
order to obviate the segregation processes that normally accom-
pany solidification of multicomponent liquids.

This memo points out other approaches that might be
considered for the preparation of superhomogeneous metallic
particles, based upon various relatively low temperature tech-
niques for the production of solid particles from liquids
containing metal cations of desired ratio which are mixed on a
molecular scale.  In some cases, these methods have been de-
veloped for applications in other areas, such as food process-
ing and the preparation of certain high performance ceramics.

SMALL PARTICLE TECHNOLOGY

R. L. Coble

## ABSTRACT

Vaporization of candidate super alloys should be used to produce homogeneous small crystallite sized powders for HIP processing in order to show what limits in property improvements can be achieved from the ultimate possible dispersion of the constituents in the starting powder.

# THEORY OF DENDRITE SOLIDIFICATION
## DURING VERY RAPID COOLING

M. C. Flemings

## ABSTRACT

A discussion is first given of heat flow in cooling and solidification of atomized liquid droplets. At high relative velocities between particle and gas, extremely rapid cooling and solidification rates are possible. At least to moderately high cooling rates (perhaps $10^4$ °C/sec or higher) solidification of alloy droplets can probably be described by simple classical expressions and the relation between dendrite arm spacing and cooling rate can be understood using concepts developed from solidification studies on samples cooled at $10^2$ °C/sec and lower.

At higher cooling rates the "classical" approach is probably not applicable and different types of structure and segregation behavior are expected.

# PRESSURE IN A SPHERICAL CAVITY OR ON A
# SOLID SPHERE IS LIMITED BY INSTABILITY

D. C. Drucker

## ABSTRACT

Hope has been expressed that truly enormous pressures
can be contained in a spherical cavity or applied to a solid
sphere through brute force or a clever variation of the auto-
frettage techniques used in gun barrels and high pressure
devices.  Certainly, no matter how high the pressure, mechanics
solutions can be written down that satisfy the stress-strain
relations for elastic and plastic material along with the
equations of equilibrium and compatibility.  For example,
calculated maximum pressure $p_a$ for a cavity of radius $\underline{a}$ in a
fully plastic sphere of outer radius b is $2\sigma_y \ln(b/a)$ assuming
a perfectly plastic material with yield strength $\sigma_y$.  In prin-
ciple, b and therefore $p_a$ can increase without limit.

However, this result is misleading because the equil-
ibrium configuration is unstable beyond a limiting pressure.
The analogy is to a long column under axial compression.  All
the equations are satisfied by a solution which takes the
column to be perfectly straight and under uniform compressive
stress.  Yet a long column will buckle well before the yield

strength is reached. Similarly, the radius $\underline{a}$ of the spherical cavity will increase indefinitely once a limiting pressure is reached. The equilibrium solution for higher pressures is unstable. A contained solid sphere under higher pressure would expand outward until the pressure dropped to the limiting value.

An easily found upper bound to a continually increasing pressure is

$$p_a = \frac{2}{3}\sigma_y \left[ 1 + \ln \frac{E}{(1+\nu)\sigma_y} \right]$$

which, when Poisson's ratio is 1/2, agrees with Hill's form for the pressure needed to expand a spherical hole in an infinite body

$$p_a = \frac{2}{3}\sigma_y \left[ 1 + \ln \frac{E}{3(1+\nu)\sigma_y} \right] \quad .$$

Work hardening increases the limiting pressure somewhat but the maximum pressure that can be contained in most materials is less than $5\sigma_y$.

The result for a cylindrical cavity is a somewhat smaller but comparable pressure. Of course, practical difficulties of any construction will reduce the maximum pressure appreciably below the theoretical limit.

A FLUID THERMAL SWITCH

H. Reiss

ABSTRACT

A phenomenon observed in a diffusion cloud chamber in
which two states of apparently stable thermal conduction have
been observed when the same temperature gradient is impressed
across a thin layer of liquid and a thicker layer of gas in
contact with it is analyzed conceptually. Although the system
is heated from below, the gas remains mechanically stable while
the liquid undergoes cellular convection. It is shown that such
thermal "switching" is possible if the effective thermal conduc-
tivity of the liquid layer possesses a region of negative slope
(with respect to temperature gradient impressed across the liquid).
Furthermore, the two states of thermal conductivity will then be
locally stable.

The switching is thought to be connected to a transition
between one mode (excitation) of cellular convection and another.
Switching in the cloud chamber is associated with fairly violent
cooling (as in boiling) of the liquid layer.

# TIGHT BINDING THEORY OF METALLIC ADHESION

W. Kohn and R. Gomer

## ABSTRACT

Metallic interfacial energies, e.g., grain boundary energies or adhesive energies between identical or different metals are of great importance in materials problems such as adhesion, wear, crack growth and strength of multiphase alloys. To our knowledge this problem has so far only been attacked in terms of the density-functional formalism which is suitable mainly for simple, i.e., non-transition metals. We have attempted to formulate the theory of interfacial energy between two (identical or different) metals in tight binding approximation for the case of simple cubic lattices without mismatch. For this purpose each infinite bulk phase and each phase including a surface are first treated using a Hartree Hamiltonian (i.e., neglecting exchange and correlation) and are then allowed to join. Particular attention is paid to self consistency which gives rise to dipole layers at the surface and at the interface. The latter dipole potential is essential for establishing a common Fermi level in the system.

This provides the groundwork for an explicit calculation of interfacial energy, by the method of moments of the density

of states. A model calculation for the case of two half-filled
bands, limited to second moments, is carried out.

The parameters entering the theory consist of the diagonal
and nearest neighbor off-diagonal matrix elements of the Hamiltonian.
The terms relevant to the interface consist of a hopping integral
coupling atoms of the two different metals and two modified di-
agonal shifts. For many applications the hopping integral will
be the important parameter. It can be estimated from the corres-
ponding integrals for the bulk metals and the overlaps of nearest-
neighbor wave functions within each metal (a) and (b) and between
(a) and (b) atoms at the interface. It seems probable that it can
be obtained from monolayer adsorption measurements.

It is expected that these calculations can be extended to
fcc and bcc structures and that mismatch at the interface can also
be taken into account.

# EFFECT OF ELECTROLYTE ON DIPOLE LAYER POTENTIALS
## AT A LIQUID-SOLID OR LIQUID-AIR INTERFACE

R. Gomer and H. Reiss

## ABSTRACT

Recent experiments in R. Gomer's laboratory measure
absolute half cell emfs to within the uncertainty posed by the
possible existence of a dipole layer at an $H_2O$-air interface
which would cause the electrostatic potential in the interior
of the $H_2O$ phase to differ from that at its free surface. Such
a dipole layer has been postulated on the grounds that the total
free energy of the $H_2O$ phase could be lowered by non-random
orientations of $H_2O$ molecules near the surface. A knowledge of
absolute half cell emfs is of importance to electrochemistry in
general; it provides absolute Gibbs free energies of hydration
for single ions and also allows some estimate of electric fields
at electrode surfaces. It is therefore also very relevant to
corrosion research. It is therefore of some interest to explore
the existence of the putative potential near the water-air inter-
face. Such a potential would tend to be screened out by mobile
charge, i.e., by the presence of an electrolyte, and this screen-
ing should be a function of Debye length, L, i.e., of (electro-
lyte concentration)$^{-\frac{1}{2}}$. Thus, a variation of experimental half
cell emfs with total electrolyte concentration should give some

information on whether there is an appreciable potential difference between the free surface and the interior of liquid $H_2O$.

We have calculated the effect of an electrolyte on the layer potential, which amounts to solving the Poisson-Boltzmann equation for this case. The linearized equation could be solved analytically for the cases of a fixed dipole layer potential of dipole length $\lambda$ and a potential decaying exponentially into the liquid of form $V_O(z) = V_O e^{-z/\lambda}$. The results are similar, and for the second case take the extremely simple form

$$V(0)/V_O = a/(a+1)$$

where $V(0)$ is the potential at the liquid surface after elecrolyte addition and $a = L/\lambda$.

The non-linear case was solved by computer by M. Mandel, working with H. Reiss at UCLA. The results are virtually identical with the linear solution up to $V_O g/kT \leq 10$, for small values of a, $a \leq 0.5$, but show more screening as $V_O$ and an increase.

These results indicate that a strong effect on the putative dipole layer potential at the air-$H_2O$ interface should be observed when the electrolyte concentration is varied in the range 1-0.01 M if the dipole layer length $\lambda \geq 10\overset{o}{A}$, which must almost certainly be the case.

These results are also relevant to potential drops existing at solid electrode-liquid $H_2O$ interfaces. However, it should be noted that a basic difference exists in the latter

case if the potential drop is an equilibrium potential differ-
ence, fixed by thermodynamics.  In that case the presence of an
electrolyte cannot screen out the potential, since the system
will adjust itself to maintain the equilibrium value.

Finally, the possibility of a dipole layer arising from
the electrolyte itself was investigated.  This could come about
if the change in solvation energy as ions approach the surface
differs for cations and anions because of their different sizes.
It turns out that this effect is negligible if the full dielec-
tric constant of $H_2O$ is maintained up to the surface.  If K is
reduced from 80 to 4, a potential of 80 meV for c = 0.1M could
result, but would decrease very rapidly with decreasing electro-
lyte concentration.

A MECHANISM FOR LIQUID PHASE
EPITAXIAL GROWTH OF NONEQUILIBRIUM
COMPOSITIONS PRODUCING A COHERENT INTERFACE

J. P. Hirth and G. B. Stringfellow

## ABSTRACT

A model is presented for growth by so-called pulling,
wherein an epitaxial deposit grows coherently but with a com-
position different from that which would be in bulk equilibrium
with the liquid phase from which growth occurs.  The breakdown
of coherent growth occurs when a dislocation nucleates at a
ledge at the growing solid-liquid interface.  An expression for
the critical condition for breakdown is presented.